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TECHNICAL REPORT ARCCB-TR-96014

**PROCESS MONITORING AND CONTROL OF ALUMINUM  
ANODIZING SOLUTIONS BY ION CHROMATOGRAPHY**

**SAMUEL SOPOK**

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**MAY 1996**



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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE May 1996		3. REPORT TYPE AND DATES COVERED Final
4. TITLE AND SUBTITLE PROCESS MONITORING AND CONTROL OF ALUMINUM ANODIZING SOLUTIONS BY ION CHROMATOGRAPHY				5. FUNDING NUMBERS AMCMS No. 6226.24.H191.1
6. AUTHOR(S) Samuel Sopok				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army ARDEC Benet Laboratories, AMSTA-AR-CCB-O Watervliet, NY 12189-4050				8. PERFORMING ORGANIZATION REPORT NUMBER ARCCB-TR-96014
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army ARDEC Close Combat Armaments Center Picatinny Arsenal, NJ 07806-5000				10. SPONSORING / MONITORING AGENCY REPORT NUMBER
11. SUPPLEMENTARY NOTES Presented at IICS'95, Grand Kimpinski, Dallas, TX, 1-5 October 1995. Published in <i>Journal of Chromatography</i> .				
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.				12b. DISTRIBUTION CODE
13. ABSTRACT (Maximum 200 words)  Process monitoring and control of sulfuric and oxalic acids in aluminum anodizing solutions are necessary to produce high-quality coatings for the metal finishing industry efficiently. These high-quality coatings significantly increase resistance to corrosion, wear, and abrasion. The production of military armament system parts requires narrow aluminum anodizing solution tolerances, which increases the need for process monitoring and control. Current instrumental analysis methods do not provide acceptable 95% confidence level precisions for these narrow operating tolerance aluminum anodizing solutions. This report describes an improved ion chromatographical method to provide acceptable process monitoring and statistical control of narrow operating tolerance aluminum anodizing solutions required to produce high-quality coatings. The resultant means and improved 95% confident precisions for typical aluminum anodizing solutions are 160.0 $\pm$ 2.3 g/l sulfuric acid and 16.0 $\pm$ 1.1 g/l oxalic acid, which are both more than a factor of two improvement over current 95% confidence level precisions.				
14. SUBJECT TERMS Process Monitoring, Sulfuric Acid, Oxalic Acid, Aluminum Anodizing Solutions, Coatings				15. NUMBER OF PAGES 10
				16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL	

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## INTRODUCTION

Inadequate monitoring of sulfuric and oxalic acids in anodizing solutions is a serious problem, resulting in poor quality and wasted resources. These acid concentrations affect conductivity, solubility, wear resistance, oxide coating thickness, porosity, and hardness. This is especially true for the narrow tolerances required to anodize armament systems. For anodizing solutions, the optimum operating ranges are 150-170 g/l sulfuric acid and 11-21 g/l oxalic acid. Current online and offline instrumental analysis methods either do not provide acceptable precisions or are time-consuming.<sup>[1-4]</sup> This report describes a similar method that improves on an existing ion chromatographical method to provide acceptable monitoring and control of these acids in the anodizing process. The report also presents an extensive statistical evaluation of the experimental data.

## EXPERIMENTAL PROCEDURE

Details are provided of the experimental procedures, materials, and apparatus used. Strict analytical chemistry methods and procedures are followed throughout this experimental section.<sup>[5]</sup>

Model 2020i Dionex Ion Chromatograph (Dionex Corporation, Sunnyvale, CA) was used. This unit includes an autosampler, computer/controller, computer/integrator, and suppressed conductivity detector.<sup>[6]</sup>

A 5-ml sample is used for the autosampler. A 2.3-ml/min eluent flow rate is used for the analytical pump. A 30- $\mu$ S output range is used for the conductivity detector. The advanced chromatography module uses an HPIC-AG4 separator column (Dionex), AMMS suppressor column (Dionex), 5-ml/min regenerate flow rate, and 10- $\mu$ L injection loop. The conductivity detector is calibrated to 147- $\mu$ S using 0.00100 M potassium chloride.

The initial scheduling conditions for the system computer/controller module's equilibration (30 min), analysis (10 min each for alternating standards S and samples A), and halt programs are 1, 18, and 1 iterations, respectively.

An analytical reagent grade solution is required for standard S containing  $160 \pm 1$ -g/l sulfuric acid and  $16.0 \pm 1.0$  g/l oxalic acid. This standard solution is prepared and standardized using previous methods developed by this author and others.<sup>[7-10]</sup> Two other reagent grade solutions are required: a 0.00095 M ( $0.100 \pm 0.005$  g/l) sodium carbonate eluent solution and a 0.0141 M ( $1.38 \pm 0.04$  g/l) sulfuric acid regenerate solution.

Preparation of an anodizing solution standard for ion chromatographic analysis requires that 1-ml of the analytical reagent grade standard solution (sulfuric and oxalic acid mixture) prepared above is diluted to the mark with deionized water in a 500-ml volumetric flask. Split sample solutions are prepared the same. This 1:500 dilution, coupled with the use of a 10- $\mu$ L injection loop, results in mean injection concentrations of 320-ppm sulfuric acid and 32.0-ppm oxalic acid.

Anodizing solution sample A is split into solutions A<sub>1</sub> and A<sub>2</sub>. The anodizing solution standard S and samples A<sub>1</sub> and A<sub>2</sub> are placed in the autosampler in 18 sealed 5-ml vials as follows:

- 4 S's for equilibration
- 3 S/A<sub>1</sub> pairs for analysis
- 3 S/A<sub>2</sub> pairs for analysis
- An S
- Deionized water

A chromatograph is generated for each anodizing standard and sample solution, peak heights are determined, standard concentrations are identified, and sample concentrations and precisions are calculated using an extensive statistical method for reliability determinations.

## RESULTS AND DISCUSSION

A statistical analysis is necessary to determine the reliability of the experimental ion chromatographic sample data in order to adequately monitor a given acid in the anodizing process. The statistical evaluation has two parts.

In the first part, samples are split, each split solution is analyzed in triplicate, and data from these split solutions are statistically compared. Figure 1 shows a typical anodizing solution chromatograph with its large sulfuric acid peak and much smaller oxalic acid peak.

Table 1 gives the experimental mean peak height X<sub>3</sub> for each of the acid standards S and split sample solutions A. The sample standard deviation S<sub>n-1</sub> is calculated for each of these samples and its associated standard. The pooled sample standard deviation S<sub>p</sub> is calculated from the standard deviation of each sample and its associated standard as follows:

$$S_p = [ (S_{n-1}^2 + S_{n-1}^2) / 2 ]^{0.5} \quad (1)$$

In addition, the 95% percent confidence level, C<sub>95%</sub>, in grams per liter is calculated from the above quantities for each sample and its associated standard:

$$C_{95\%} = (2.266)(S_p)[\text{acid std conc} / X_3] \quad (2)$$

Figures 2 and 3 give typical respective sulfuric acid and oxalic acid calibration and 95% confidence level data. The 95% confidence data in these figures agrees with the 95% confidence data calculated by equation (2) and given in Table 1.

Finally, the mean retention time ( $t_R$ ) in minutes is given for each standard and split sample solution.

The concentration data of the split sample solutions are given in Table 2. As above, the mean  $X_3$ , sample standard deviation  $S_{n-1}$ , and pooled sample standard deviation ( $S_p$ ) are calculated. In addition, another quantity is calculated: the T-test value (T) for each sample solution from the following:

$$T = (1.225) [ (X_3 - X_3) / S_p ] \quad (3)$$

The experimental data of the split solutions of a sample solution are compared with a 2.776 value using the T-test. The T-test determines if these split solutions are statistically from the same original sample solution to a 95% confidence level. A sample solution passes the test if its resultant absolute value is less than the 2.776 value. The T-test resolves the reliability dilemma mentioned above, since it either accepts or rejects a sample solution analysis. Sample solutions that fail the test are statistically dissimilar and are resampled and reanalyzed.

In the second part, the mean  $X_6$  and normal population standard deviation ( $S_n$ ) are calculated for the six respective replicates of the sample solutions that have passed the T-test. Since this was the case, the concentration data for the unsplit and original sample solutions are also given in Table 2.

Previously, the variations in precision were examined for the materials, methods, and instrumentation used. Clearly, the ion chromatographic system contributes the greatest amount of variation in precision compared with all other sources given for both anodizing acid constituents.<sup>[10]</sup>

For the 20-g/l sulfuric acid operating tolerance band in these anodizing solutions, the 95% confidence level improved precision is about  $\pm 2.3$  g/l compared with the current  $\pm 5.1$ -g/l value.

For the 10-g/l oxalic acid operating tolerance band in these anodizing solutions, the 95% confidence level improved precision is about  $\pm 1.1$  g/l compared with the current  $\pm 2.3$ -g/l value.

The 95% confidence level precision bands in Figures 2 and 3 collapse by more than a factor of two when this improved statistical method is used. For each acid, this improved statistical analysis allows more than twice as many precision bands to fit within its corresponding tolerance band. This improvement results in a controllable armament anodizing system.

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**Table 1. Peak Height Data for Acids in Typical Anodizing Solutions**

	$S_1$	$A_1$	$S_2$	$A_2$
$H_2SO_4$				
$X_3(\mu S)$	15.73	14.98	15.73	14.85
$S_{n-1}(\mu S)$	$\pm 0.26$	$\pm 0.20$	$\pm 0.13$	$\pm 0.23$
$S_p(\mu S)$	--	$\pm 0.23$	--	$\pm 0.19$
$C_{95\%}(g/l)$	--	$\pm 5.57$	--	$\pm 4.64$
$t_R(min)$	2.99	2.99	2.99	2.99
$H_2C_2O_4$				
$X_3(\mu S)$	1.702	1.615	1.722	1.617
$S_{n-1}(\mu S)$	$\pm 0.098$	$\pm 0.098$	$\pm 0.098$	$\pm 0.110$
$S_p(\mu S)$	--	$\pm 0.098$	--	$\pm 0.104$
$C_{95\%}(g/l)$	--	$\pm 2.20$	--	$\pm 2.33$
$t_R(min)$	4.80	4.80	4.80	4.80

**Table 2. Concentration Data for Acids in Typical Anodizing Solutions**

	$\text{H}_2\text{SO}_4\text{A}_1$	$\text{H}_2\text{SO}_4\text{A}_2$	$\text{H}_2\text{C}_2\text{O}_4\text{A}_1$	$\text{H}_2\text{C}_2\text{O}_4\text{A}_2$
$X_3(\text{g/l})$	152.4	151.0	15.20	15.02
$S_{n-1}(\text{g/l})$	$\pm 0.8$	$\pm 1.2$	$\pm 0.80$	$\pm 0.18$
$S_p(\text{g/l})$	--	$\pm 1.0$	--	$\pm 0.58$
T	--	1.7	--	0.38
$X_6(\text{g/l})$	--	151.7	--	15.11
$S_n(\text{g/l})$	--	$\pm 1.2$	--	$\pm 0.53$
$S_{95\%}(\text{g/l})$	--	$\pm 2.3$	--	$\pm 1.06$

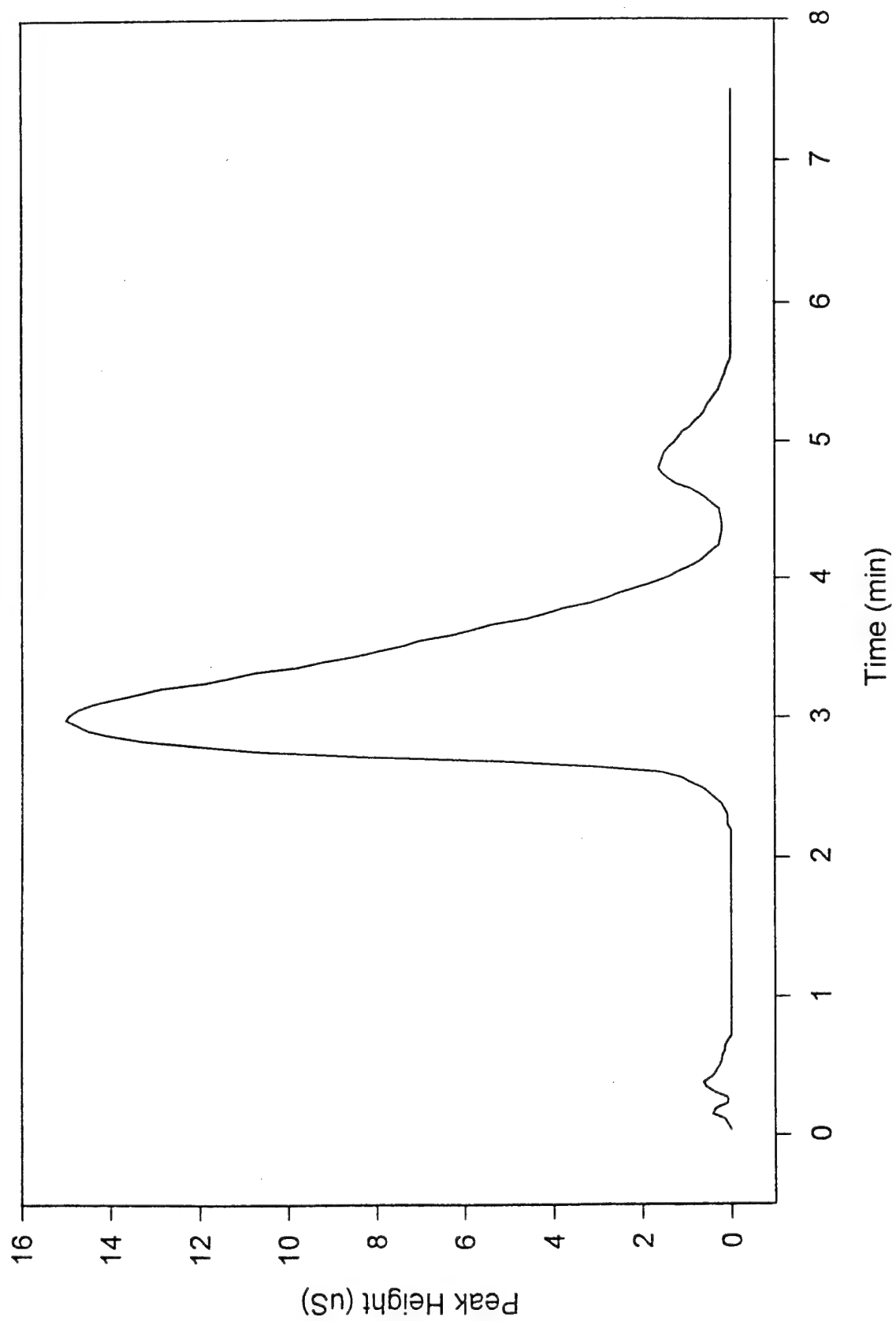


Figure 1. Typical anodizing solution chromatograph

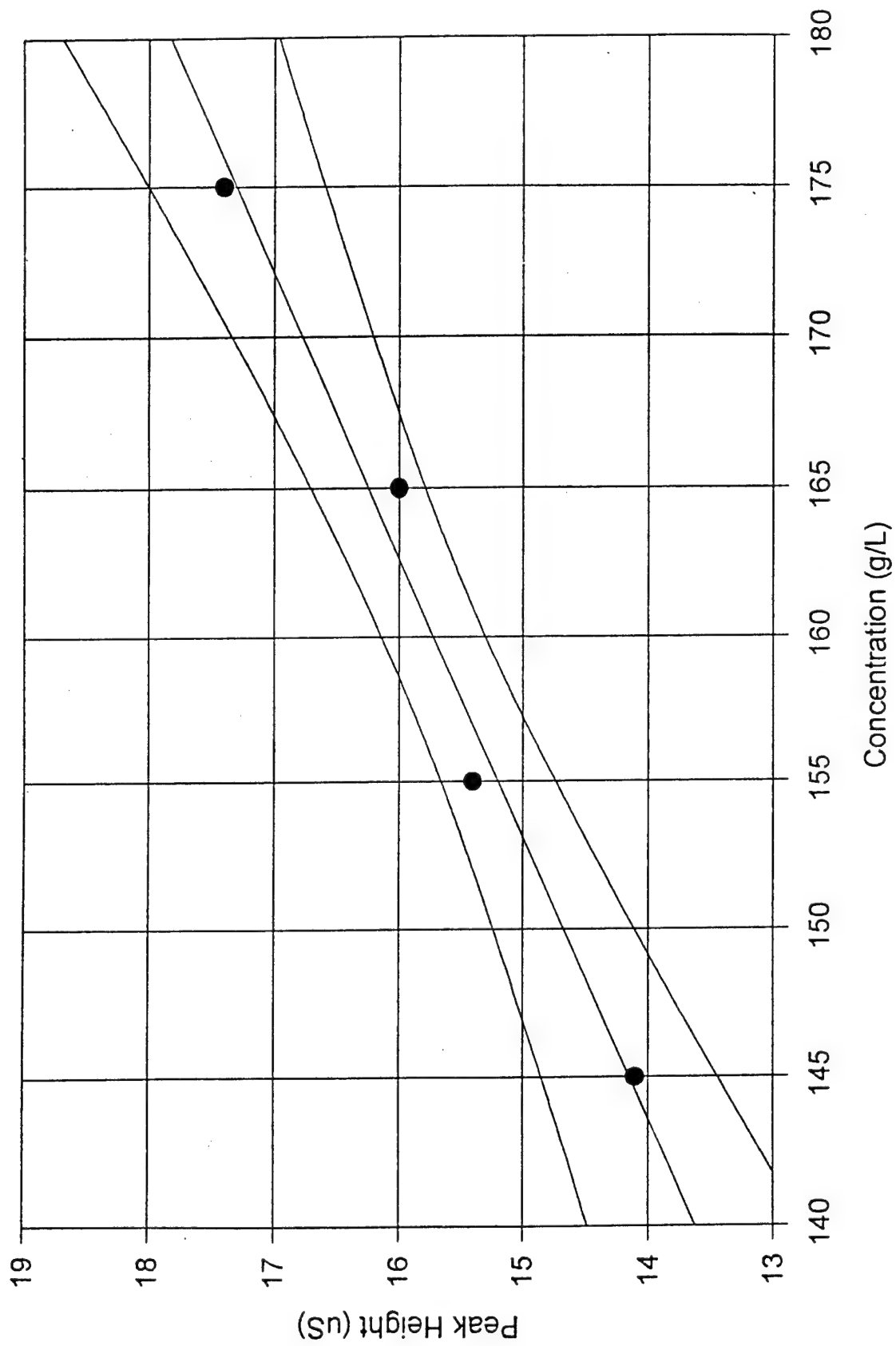


Figure 2. Typical sulfuric acid calibration and 95% confidence data

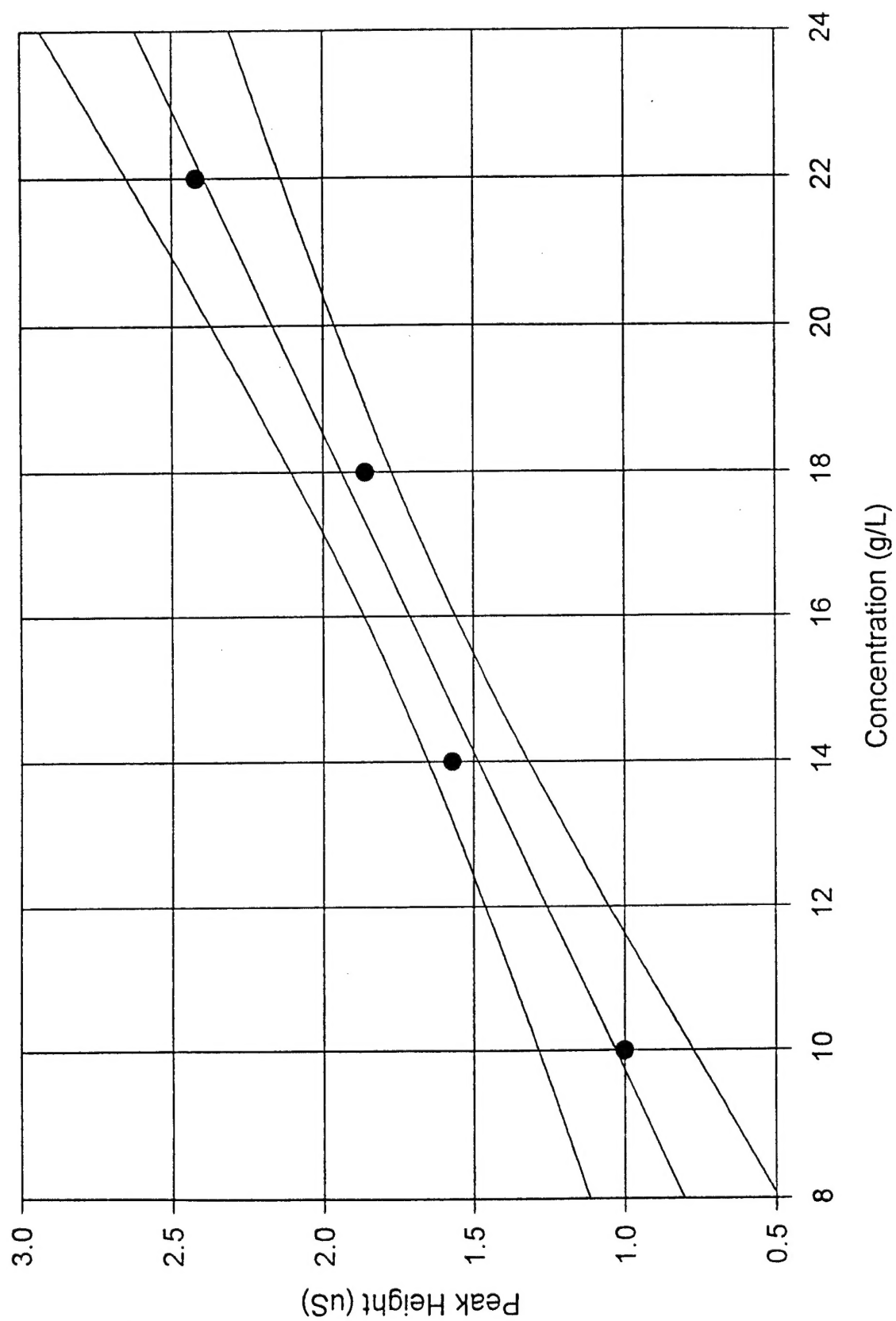


Figure 3. Typical oxalic acid calibration and 95% confidence data

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